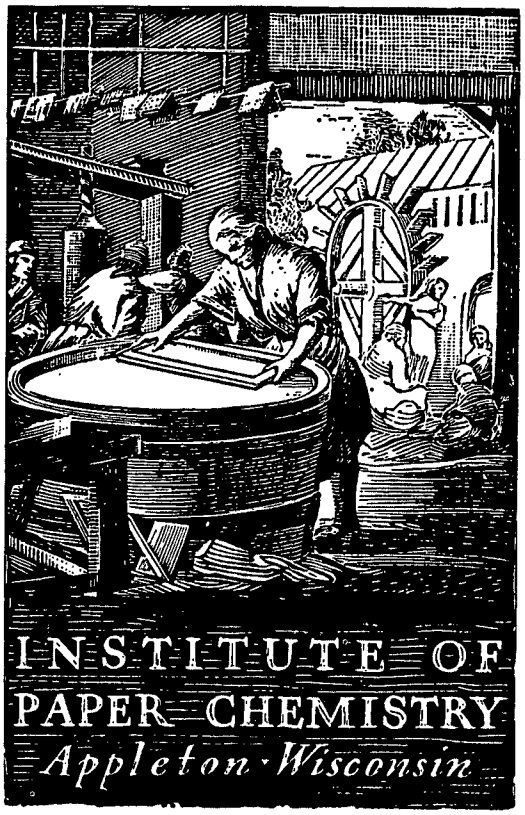

POLYCHLORINATED BIPHENYLS IN PULP AND PAPER MILLS
PART I. ANALYTICAL METHODOLOGY

Project 3295

Report One
A Progess Report
to
MEMBERS OF THE INSTITUTE OF PAPER CHEMISTRY

September 3, 1976

THE INSTITUTE OF PAPER CHEMISTRY

Appleton, Wisconsin

POLYCHLORINATED BIPHENYLS IN PULP AND PAPER MILLS

PART I. ANALYTICAL METHODOLOGY

Project 3295

Report One

A Progress Report

to

MEMBERS OF THE INSTITUTE OF PAPER CHEMISTRY

September 3, 1976

TABLE OF CONTENTS

THE INSTITUTE OF PAPER CHEMISTRY

Appleton, Wisconsin

POLYCHLORINATED BIPHENYLS IN PULP AND PAPER MILLS
PART I. ANALYTICAL METHODOLOGY

SUMMARY

Concern over the entry of polychlorinated biphenyls (PCB's) into the environment has generated the need for accurate determinations of PCB's in pulp and paper mill effluents. Differences between test results obtained in different laboratories have demonstrated that there are inadequacies in the currently available analytical methodology. Therefore, the objective of this investigation has been to develop more accurate procedures for determining PCB's in effluents and fiber slurries from within the mill. Specific tasks comprising this objective include: (a) To learn how to extract completely all of the PCB from slurries containing cellulose fibers. (b) To determine effects of surfactants and surface area of cellulose on the distribution of PCB's between water and fibers. (c) To learn ways of removing or avoiding interferences on PCB gas chromatograms.

Oxidation with chromium trioxide was found to be the most effective technique for removing interfering materials from PCB chromatograms. Some materials not removed by this treatment were determined not to be PCB's. Errors in PCB quantitation caused by these materials can be reduced if the analyst ignores peaks which do not conform to a known PCB pattern in both retention time and relative peak height.

Because it is apt to give erroneous and misleading results, perchlorination is not a suitable means for confirming the presence or quantity of PCB's in effluents from mills using secondary fiber.

Addition of the commercial PCB mixture, Aroclor 1242, to aqueous suspensions of cellulose fibers resulted in distribution of the PCB between the cellulose and the water. In contrast with long fibers, greater amounts of PCB were sorbed onto fiber fines, presumably because of their greater surface area. Small amounts of the nonionic surfactant, Triton X-100, had only a small effect on the distribution, but larger amounts (> 0.01%) promoted removal of PCB from the slurry by separatory funnel extraction with petroleum ether.

Although recoveries of PCB added to water samples ranged from 86 to 100%, typical recoveries of Aroclor 1242 added to fiber slurries were lower (60-80%). A search for origins of the PCB losses which produced the low recoveries has revealed that: (a) Aroclor 1242 can apparently be readily lost from aqueous solutions by volatilization. (b) Aroclor 1242 can be lost from isolated fibers if they are permitted to air dry at room temperature. (c) Low recoveries reflect actual PCB losses rather than PCB which could not be removed from the fibers.

To avoid volatilization losses, an effective PCB isolation procedure should involve minimal manipulation and exposure of aqueous samples to the atmosphere.

Based on the above findings an improved procedure for determining PCB's in pulp and paper mill effluents and process streams is proposed (see Recommendations).

INTRODUCTION

Polychlorinated biphenyls (PCB's) are compounds formed by the chlorination of biphenyl. Commercial PCB's, manufactured domestically by Monsanto, are sold as mixtures called Aroclors. Aroclors are high boiling liquids or resinous solids. They have low chemical reactivity and water solubility, and they will not support combustion. Over the years PCB's have found uses in transformers and capacitors, as heat-transfer fluids, and as plasticizers in paints, coatings, and caulking materials. With the advent of carbonless copy paper, Aroclor 1242 was used within the capsules as the carrier for the dye.

Since 1968, evidence has been accumulating which suggests that PCB's possess low-level, but significant, toxicity (1). As a result of their wide and varied usage, these compounds have become universally distributed throughout the environment. Because of their stability and oil-solubility, PCB's tend to accumulate to multi-ppm levels in the flesh of fish and other wildlife. PCB residues in fish do not appear to be declining in spite of Monsanto's 1971 limitation of PCB use to closed systems and the termination of PCB use in carbonless copy paper (2).

Human intake of PCB's appears to result principally from consumption of freshwater fish (3). A recent study revealed that consumers of large quantities of sport-caught (and presumably high PCB content) fish from Lake Michigan suffered no greater incidence of medical problems than did members of a control group (4). The fish eaters did, however, have elevated PCB levels in their blood. Although the long-term human toxicity of environmental levels of PCB remains in doubt, these compounds have nevertheless become one of today's environmental pollutants of greatest concern.

Current paper industry involvement with PCB's arises almost exclusively from the use of recycled fiber. Carbonless copy paper containing Aroclor 1242, made prior to the spring of 1971, is apparently still entering the recycling stream. This Aroclor 1242 enters the mills using recycled fiber with their raw material and leaves in their products, effluents, and sludges.

The industry's initial concern with PCB's was prompted by the Food and Drug Administration's proposed temporary tolerance of 5 ppm (later 10 ppm) PCB in paperboard food packing. Paperboard manufacturers responded by greatly reducing the PCB content of their products. This was achieved principally by rejection of all types of wastepaper suspected to contain PCB's (5).

Most recently, amounts of PCB's in effluents from paper mills using secondary fiber have become a major concern. Legislation designed to regulate the entry of PCB's into the environment via aqueous effluents has been enacted or is pending in several states. For many paper manufacturers, in contrast with board manufacturers, control of PCB input into the mill by avoiding all wastepaper grades in which it is apt to be found is economically impractical. Consequently, methods for removal of PCB's from effluents or from process streams within the mills will have to be adopted. Accurate measurements of PCB's in process streams and effluents are necessary in order to determine the extent of a mill's PCB problem and to assist in the selection and evaluation of control technology. Development of analytical methods needed for performing the PCB determinations is the principal objective of this current investigation.

ANALYTICAL METHODOLOGY AND TEST VARIATION

The most widely accepted methods for PCB determination involve extraction of the PCB from the sample with a nonaqueous solvent, cleanup of the extract by adsorption chromatography on alumina or Florisil, and analysis on a gas chromatograph with an electron capture detector. Hutzinger, et al. (6) have reviewed the many variations of this procedure as devised for the analysis of different types of samples.

Gas chromatography — mass spectrometry (GC/MS) of PCB's has been used principally to obtain qualitative information, i.e., to confirm that a sample actually does contain PCB's. Quantitative PCB determinations have also been performed using GC/MS with computer controlled repetitive data acquisition from selected specific ions (7). However, the mass spectrometer — minicomputer combination needed to quantitate nanogram levels of PCB's constitutes a significant obstacle to immediate wide application of that technique.

Reflux with alcoholic KOH is used to extract PCB's from paper and paperboard (8). Results of a collaborative study of this method were sufficiently precise to support its adoption by the Association of Official Analytical Chemists (9). In an investigation of sources of between-laboratory variation in the determination of PCB's in paperboard (10) significant potential PCB losses were found to occur during its extraction from paperboard and sample cleanup. Use of different techniques for obtaining quantitative data from electron capture gas chromatograms was an additional source of variation. Limitations on testing accuracy and precision resulting from chromatogram quantitation were described by Hutzinger, et al. (11) as follows:

> "The quantitation cannot be accurate since it is not based on a complete resolution of all chlorobiphenyls, and quantitative detector responses to all the chlorobiphenyls are not known. However, the quantitation can be precise and the degree of precision, tested in a multilaboratory exchange-sample program, is about the same as the precision and accuracy of the determination of the common chlorinated hydrocarbon pesticides (standard deviation ± 20%)."

Improved accuracy and precision should result from use of the individual peak integration method of Webb and McCall (12), but that procedure is probably too time-consuming for routine manual application.

Collaborative studies have revealed large between-laboratory variations in determinations of PCB's at levels commonly found in water and effluents. An Environmental Protection Agency (EPA) study involving several laboratories yielded results ranging from 0.82 to 2.2 ppb on a water sample containing 1.5 ppb (13). The EPA-recommended method for PCB's in effluents (14) was used in that investigation; the method employs a silica gel microcolumn to separate PCB's from organochlorine pesticides if they are present in the sample. The ASTM method for PCB's in water, D 3304-74, has also been tested collaboratively. At low PCB levels, 1-20 ppb in distilled water and river water, participating laboratories agreed within a factor of two (15). Because significant amounts of PCB were lost (for unknown reasons) during 3-4 weeks' storage between sample preparation and analysis, it was impossible to determine the accuracy of the method (15). Formaldehyde, a preservative recommended by Bellar and Lichtenberg (16), had not been added to the samples.

As shown in Table I, PCB measured in industrial effluents was quite variable even when formaldehyde preservative was used. These data are believed to be typical of the responses received whenever split effluent samples are submitted to several laboratories for analysis. Likely contributors to the scatter

in the data were variations in instrumentation, laboratory technique, and chromatogram interpretation. In addition, results might have been affected by sample degradation (even with preservatives), incomplete extraction of the PCB from the sample, and interferences on the chromatogram.

TABLE I

PCB CONTENTS, µG/LITER, MEASURED IN REAL AND SYNTHETIC EFFLUENTS BY DIFFERENT LABORATORIES

	Sample					
Laboratory	1[a]	2[a]	3	4	5[b]	6[b]
A	19, 16	<0.1	102	0.3	9.8	7.7
B	9.4, 11.8	2.5	21.5	1.5	--	--
C	12, 10	<0.5	--	--	--	--
D[c]	--	--	180	0.6	--	12
E[c]	--	--	--	--	20	--
True value	25	0	NA	NA	NA	NA

[a] Spiked, synthetic effluent.

[b] Interferences reported by both laboratories.

[c] Samples analyzed by Laboratory D and perhaps also Laboratory E did not contain preservative.

NA = not available.

The presence of interferences and the possible inadequacy of the common methods for determining PCB's in paper mill effluents were suspected of being the greatest potential sources of test variation. Thus, they were selected as the initial topics for investigation in this study of PCB analytical methodology.

INVESTIGATION AND DISCUSSION

INTERFERENCES IN PCB DETERMINATIONS

Typical PCB chromatograms showing interferences are illustrated by Fig. 1a, 2a, and 3b. Possible routes by which the interference problems could be resolved included: (a) Remove the PCB from the interferences, presumably by perchlorination to decachlorobiphenyl, whose retention time would be longer than the interferences. (b) Remove the interferences from the extract containing the PCB's. (c) Learn which peaks are not PCB's so that they could be ignored in evaluation of subsequent chromatograms.

Perchlorination

Perchlorination is typically used for confirming questioned PCB identifications. All of the PCB isomers in the isolated Aroclor mixture are converted to a single compound, decachlorobiphenyl (DCB), which produces a single, strong peak on the chromatogram. The perchlorination procedure studied in this laboratory is essentially that of Huckins, et al (17) as modified in unpublished work by several investigators (18). The modifications, noted in Appendix III, have been designed to promote complete perchlorination with minimized volatilization loss of Aroclor 1016 and 1242.

Perchlorination was attempted on authentic effluents from recycling mills as well as on distilled water containing Aroclor 1242 plus other suspected high-boiling components of recycled carbonless copy paper (alkyl biphenyls and alkyl naphthalenes). Reaction mixtures consistently charred, and low DCB yields were obtained from the spiked samples. This result agreed with the finding in another laboratory where other high-boiling compounds, polynuclear aromatic hydrocarbons, charred and reduced the DCB yield (19). Because the high-boiling

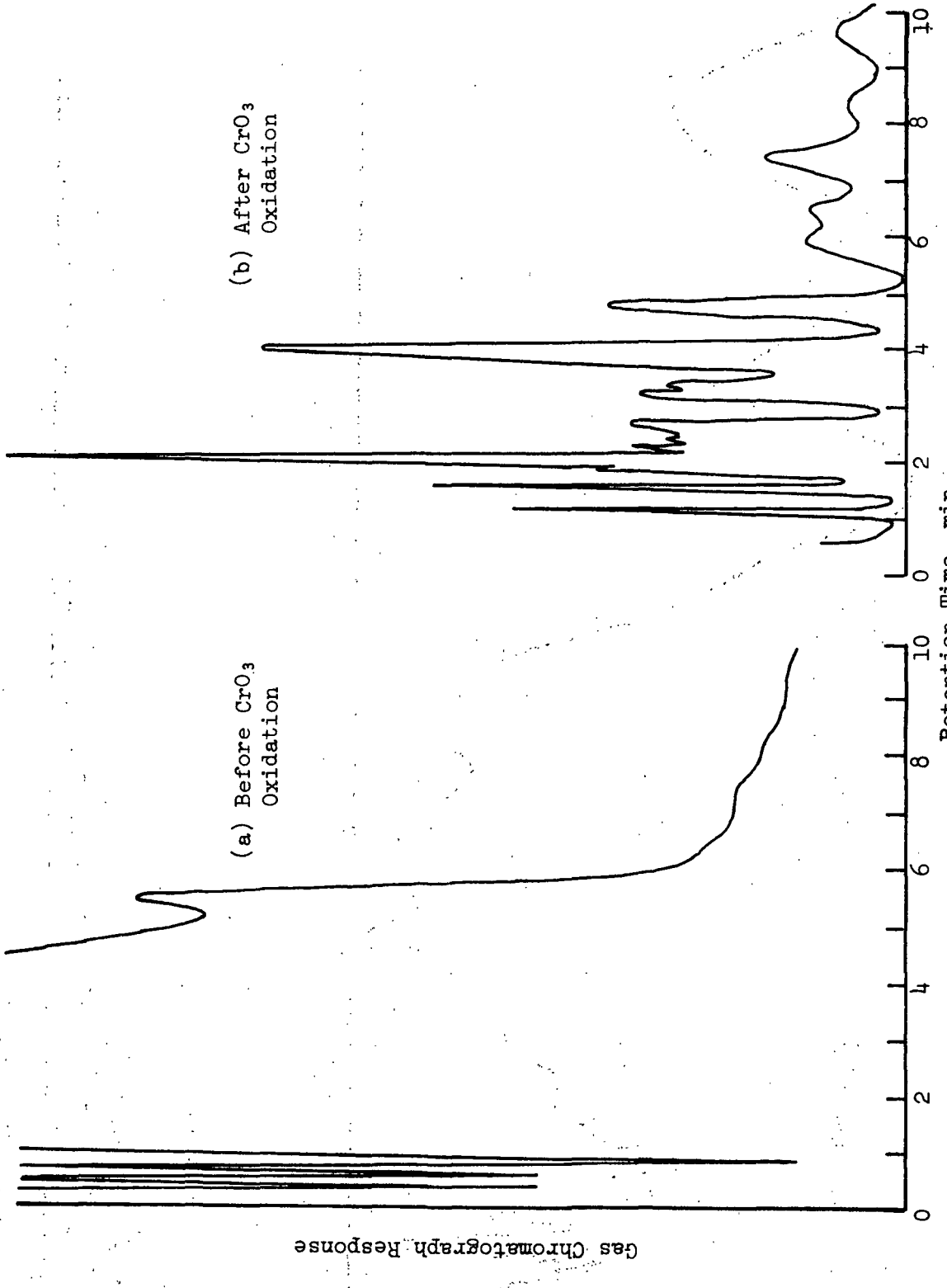

Figure 1. Pulp Mill Effluent Spiked with Aroclor 1242

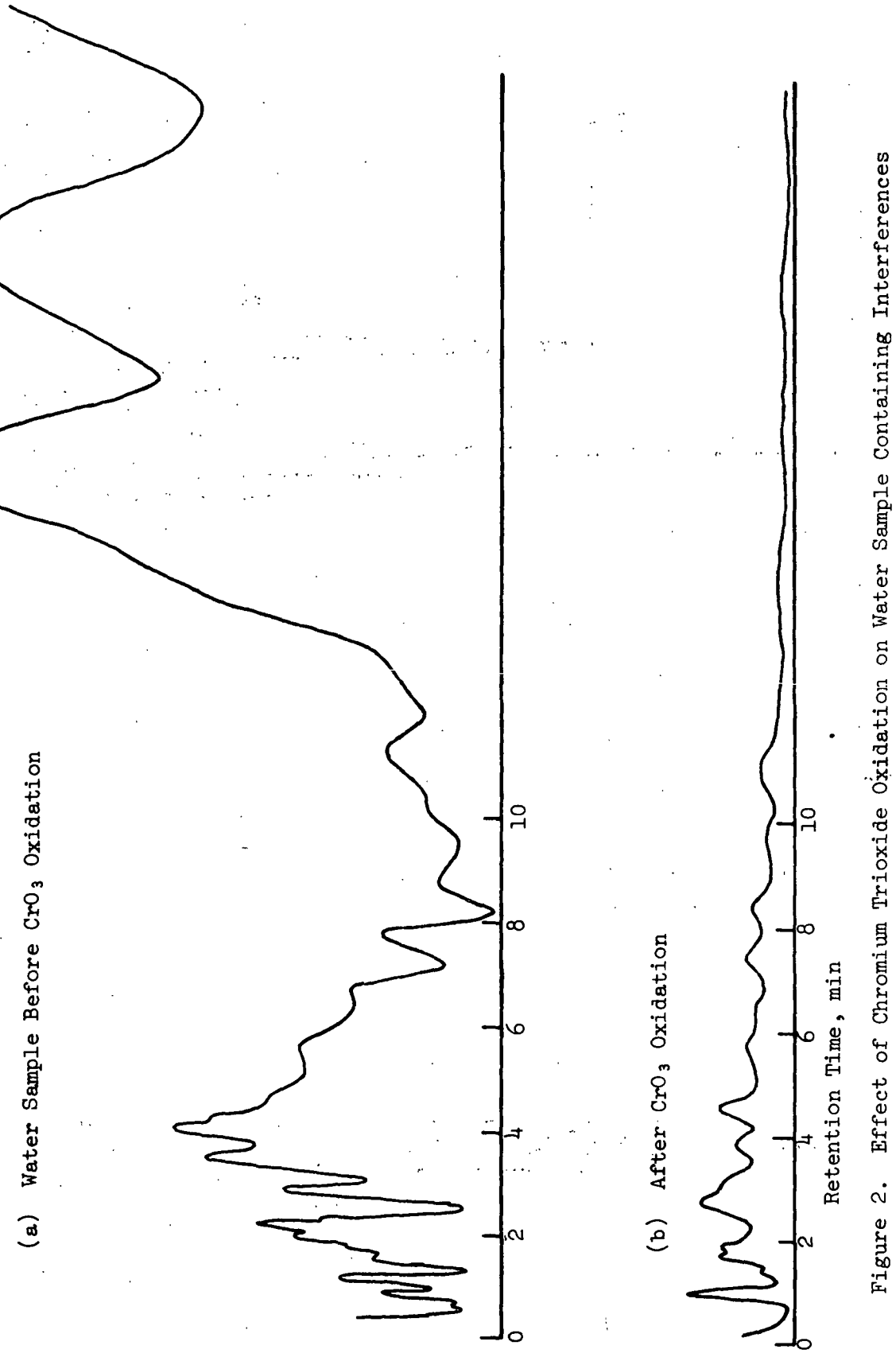

Figure 2. Effect of Chromium Trioxide Oxidation on Water Sample Containing Interferences

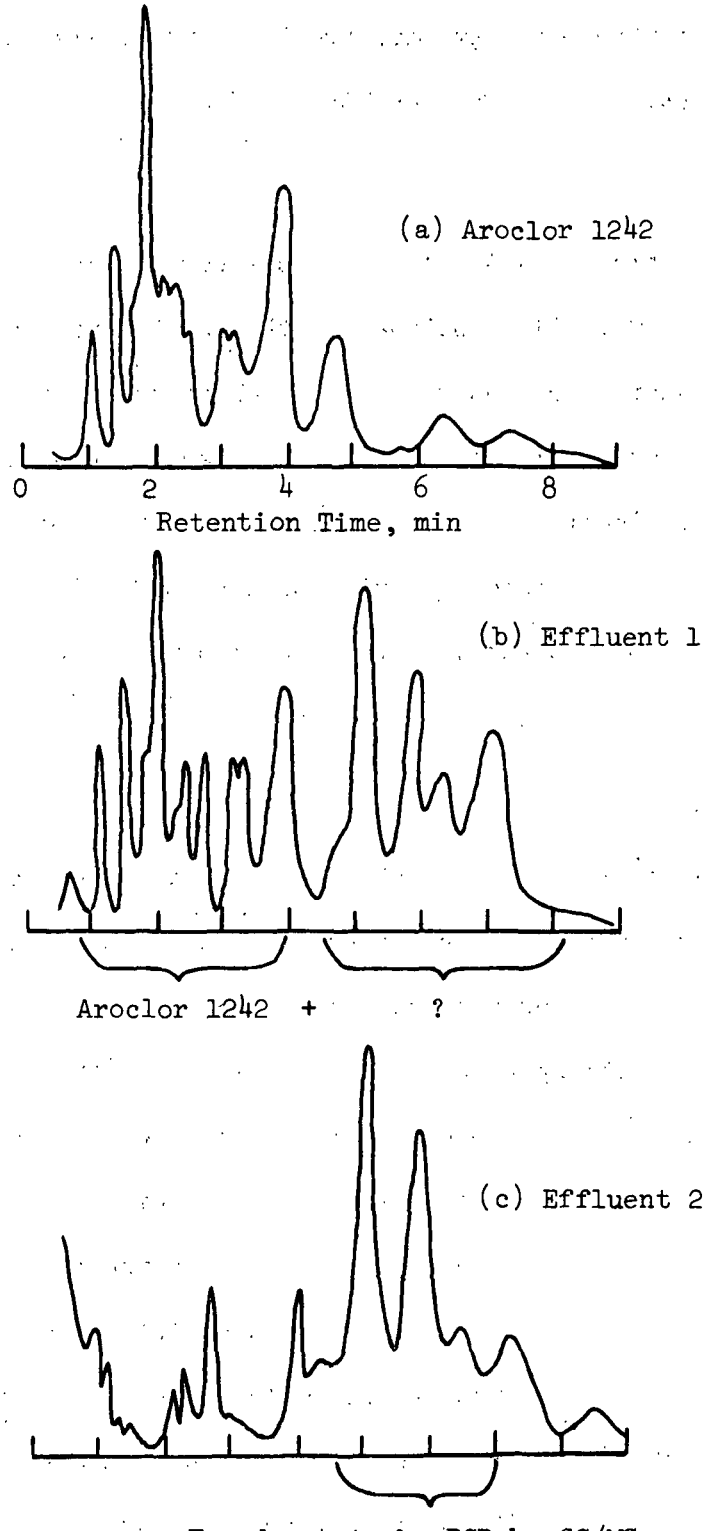

Figure 3. An Interference Identification Problem Solved by Gas Chromatography-Mass Spectrometry

constituents of modern carbonless copy paper would quite likely be predominant over PCB's in an effluent, their effect on DCB yield greatly reduces the utility of perchlorination.

The same alkyl biphenyls and naphthalenes were subjected to perchlorination in the absence of PCB. Also included in this series was unsubstituted biphenyl. Reaction products were analyzed by gas chromatography using temperature programming to improve peak resolution. Amounts of sample injected were sufficient for detection by flame ionization as well as electron capture detectors. All samples yielded a peak with the same retention time as DCB. Thus, effluent analysis using perchlorination might incorrectly report these nonchlorinated compounds as PCB's.

Removal of Interferences

In most PCB determinations the PCB's can be adequately separated and distinguished from non-PCB materials on the basis of the PCB's solubility in organic solvents, low affinity for alumina or Florisil adsorbents, behavior in the gas chromatograph, and strong response in the electron capture detector. Interferences occur when non-PCB compounds strongly resemble PCB's in each of these properties. Removal of the interference can be achieved if the PCB's and interference can be found to differ in some additional property, such as solubility or chemical reactivity. PCB's can be separated from materials of lower polarity, such as paraffins, by virtue of the PCB's solubility in acetonitrile (20) or dimethyl formamide (21). The solubility of many classes of compounds in concentrated sulfuric acid permits their extraction from a hexane solution of PCB's (21). Other widely-used separation techniques include a silica gel microcolumn to separate PCB's from pesticides (14) and treatment with alcoholic KOH to react with and permit removal of interferences (22).

Each of the above treatments was tested on a variety of authentic samples containing interferences, such as those shown in Fig. 1a and 3b. Chromatogram appearance was used for qualitative evaluation of treatment effectiveness. In general, Fig. 1a chromatograms were not affected by the treatments, and some of the interfering peaks on Fig. 3b chromatograms were reduced but not removed.

When reports of separations employing chromium trioxide oxidation were found (23,24), that treatment was tested and found to produce the dramatic improvements illustrated by Fig. 1 and 2. The chromium trioxide apparently converts many non-PCB compounds to more polar forms which are subsequently removed on a Florisil column. PCB's do not react with the chromium trioxide, although small losses of Aroclor 1242 have occurred due to volatilization during sample concentration. Recoveries of Aroclor 1242 spikes carried through the chromium trioxide treatment have been roughly 90%. Details of this treatment are included in Appendix II.

Chromium trioxide oxidation has been successfully applied to a growing list of over 20 samples. Its greatest value is in removal of the broad peak which completely obscures the Aroclor 1242 region of some chromatograms (Fig. 1a). This broad peak has been found in many pulp mill effluents and sludges from a variety of sources, and it is thought to be due to sulfur in the sample. Alkyl naphthalenes, a possible component of newer carbonless copy paper, are also removed by this treatment, but alkyl biphenyls would not be affected. Figure 2 provides another example of the chromium trioxide treatment; peaks on the cleaned-up chromatogram were considered to represent an Aroclor 1242-1254 mixture. In general, oxidation with chromium trioxide appears to be the best way to clean up samples that give distorted chromatograms. Although not all interfering materials

are removed, peaks on chromatograms of treated samples permit more confident qualitative identification and quantitation of PCB's.

Gas Chromatography – Mass Spectrometry

Peaks similar to those on the right side of Fig. 3b have presented difficult problems for analysts because they are frequently encountered and could not be removed by any of the methods investigated, including chromium trioxide. The unknown peaks had retention times quite similar to PCB isomers found in the common Aroclors, but their relative peak heights did not match Arochlor 1248, 1254, or a 1242-1254 mixture. Thus, it was not clear whether the whole chromatogram represented a "weathered," biodegraded PCB, or alternatively, Aroclor 1242 plus interferences. The resolution of that question strongly affected PCB quantitation and has been suspected of being a significant source of between-laboratory test variation.

A method for solving the Fig. 3b identification problem with available instrumentation was provided by finding the authentic sample whose chromatogram is Fig. 3c. The principal peaks of Fig. 3c matched the unknown peaks of Fig. 3b quite well, which suggested that they represented the same materials. Because the peaks of interest in Fig. 3c were also the major peaks on the chromatogram, their analysis at the nanogram level by GC/MS was simplified. GC/MS analysis of the Fig. 3c sample was conducted at the Wisconsin Laboratory of Hygiene. Although the peaks could not be identified with certainty, it was determined that they were not PCB's. Therefore, it was concluded that the same peaks in Fig. 3b were also not PCB's and that they could be ignored in the quantitation of this and similar chromatograms.

The finding in this investigation that peaks with approximately correct retention times but incorrect relative peak heights were apparently not PCB's has

generated a conservative attitude toward chromatogram interpretation: Positive identification of a commercial PCB requires that peaks have retention times and relative peak heights that match a known Aroclor or mixture of Aroclors.

EFFECT OF SURFACTANTS AND FIBER SURFACE AREA ON PCB DISTRIBUTION

It is generally believed that in aqueous systems containing PCB's and suspended particulate material the PCB's tend to be selectively associated with the particulates. For example, transport of PCB's in upper Chesapeake Bay has been reported to occur via sorption on suspended sediment (25). Data have not been available to indicate how PCB's might become distributed between water and particulate when the particulate material is cellulose fibers. The need for such information is especially evident in two areas: (1) analytical methodology, and (2) waste treatment processes. In both cases, efficient method and process design would depend heavily upon knowing which phase contains most of the PCB.

Because they are used in the deinking of wastepaper, surfactants are likely constituents of effluents from the same mills which are apt to be concerned with PCB's. When the concentration of a surfactant exceeds its critical micelle concentration, it becomes capable of solubilizing materials of low water solubility such as PCB's. Thus, because surfactants can potentially affect the distribution of PCB's between water and suspended particulate, perhaps by exerting a detergent action to remove PCB's from the fibers, their behavior in such a system needed examination.

Initial PCB distribution results originated from spike recovery studies designed to evaluate use of separatory funnel extractions for removal of PCB's from slurries. Aroclor 1242 spikes in ethyl alcohol were stirred into 1% slurries; the spike concentration in the slurry was 100 µg/liter. The slurries were

extracted three times in a separatory funnel with 60 ml solvent. Extracts were cleaned up and analyzed as described in Appendix I. The slurries were then filtered through paper on a Buchner funnel, and the residual PCB was removed from the wet solids (plus filter paper) by alcoholic KOH reflux, as is used for isolating PCB's from paperboard (8).

Typical data from replicate samples are shown in Table II. In this and subsequent tables, values are percentages of the recovered PCB. Total recoveries, ranging from about 60 to 80%, are considered in detail in a later section of the report. Results in Table II on the hardwood pulp substitute prompted the tentative recommendation that PCB's be routinely isolated from slurries using the two-step procedure (separatory funnel extraction followed by alcoholic KOH reflux) employed in this study. In retrospect, the clay and starch detected later in the hardwood pulp substitute might have enhanced the fraction of the PCB held on the solids. Thus, those data did not present a clear indication of PCB distribution between water and cellulose fibers.

TABLE II

PCB REMOVAL BY LIQUID-LIQUID EXTRACTION

Pulp	Solvent	Extracted by Separatory Funnel, %	Remaining on Solids, %
Hardwood pulp substitute	Petroleum ether	31.2	68.8
Hardwood pulp substitute	15% CH_2Cl_2 in petroleum ether	26.8	73.2
Bleached hardwood	Petroleum ether	69.0	31.0
Most mill slurries	Petroleum ether or 15% CH_2Cl_2 in petroleum ether	$\sim$ 100	$\sim$ 0

Although there were some notable exceptions, little PCB was isolated from the solids after authentic paper mill slurries were subjected to separatory funnel extraction. The difference between that finding and the other results in Table II was puzzling, although the surfactants probably contained in the mill samples were suspected of facilitating PCB removal in the separatory funnel.

Table III shows results from a more detailed study of PCB distribution. A bleached softwood pulp was beaten and classified. Using the constant rate filtration technique (26), the hydrodynamic specific surface of the on-10 mesh fibers and the through-65 mesh fines was found to be 9,580 and 120,000 cm^2/g, respectively. Identical alcohol-benzene extractives, 0.2%, were measured on each of the two fractions. Slurries, 0.78% consistency for the long fibers and 0.425% for the fines, were spiked with 100 µg/liter Aroclor 1242. Surfactants were added at a concentration of 0.1% based on the total slurry. The slurry was stirred for three minutes after all components were added. In contrast with previous studies, these slurries were filtered prior to PCB extraction. PCB's were then removed from the wet fibers by alcoholic KOH reflux and from the filtrate by separatory funnel extraction with petroleum ether.

Data in Table III indicate that the fines adsorbed more PCB than did the long fibers. If the fines consistency had been as high as that of the fibers, that trend would quite likely have been even more emphatic. In the absence of added surfactant, the PCB adsorbed by the long fibers and fines was computed to be 1,580 and 13,700 ng/g o.d. fiber, respectively. Thus, the ratio of the amounts of PCB adsorbed by the two fractions was roughly proportional to the ratio of their hydrodynamic specific surfaces (about 1:10).

TABLE III

EFFECT OF SURFACTANTS ON PCB FIBER/WATER DISTRIBUTION

Surfactant[e]	Type	HLB[a]	Fibers	Recovery from Fibers, %[b]	Recovery from Filtrate, %[b]	Total Recovery, %
None	--	--	On 10 mesh	21.8	78.2	63.9
			Through 65 mesh	87.7	12.3	66.8
L[c]-103	Nonionic	1.5	On 10 mesh	5.8	94.2	69.4
			Through 65 mesh	60.9	39.1	76.4
X[d]-200	Anionic	10.7	On 10 mesh	3.7	96.3	53.5
			Through 65 mesh	32.5	67.5	78.7
X[d]-100	Nonionic	13.5	On 10 mesh	1.7	98.3	60.2
			Through 65 mesh	3.8	96.2	71.1
X[d]-405	Nonionic	17.9	On 10 mesh	25.9	74.1	51.7
			Through 65 mesh	80.8	19.2	70.9

[a] Hydrophile-lipophile balance.

[b] Percentage of the actual PCB recovered.

[c] Pluronic (Wyandotte Chemicals Corp.)

[d] Triton (Rohm & Haas).

[e] Added at concentration of 0.1% based on total slurry.

Prior to the study with Triton X-405, the data indicated that surfactant effectiveness in solubilizing PCB's increased with increasing hydrophile-lipophile balance (HLB). (The hydrophile-lipophile balance is an expression of the relative simultaneous attraction of a surface-active agent for water and for oil.) The anomalous results with X-405 suggest the need for additional studies to determine the mechanism by which surfactants affect PCB distribution.

Because Triton X-100 was the most effective of the surfactants studied at 0.1% concentration, it was also evaluated at lower concentrations, as shown in Table IV. Data in the table indicate that, in contrast with the effect of

0.1% X-100, the lower concentrations have only minor influence on the distribution of PCB's between fibers and filtrate. These results provide the basis for speculation that low levels of surfactants in a mill effluent will probably not seriously hinder PCB removal via suspended solids removal in an efficient clarifier. Although data on surfactants in authentic effluents are inadequate, the demonstrated efficiency of PCB removal in several operating clarifiers appears consistent with this speculation (27).

TABLE IV

EFFECT OF TRITON X-100 CONCENTRATION ON PCB FIBER/WATER DISTRIBUTION

Concentration, %	Fibers	Recovery from Fibers, %[a]	Recovery from Filtrate, %[a]	Total Recovery, %
None	On 10 mesh	21.8	78.2	63.9
	Through 65 mesh	87.7	12.3	66.8
0.003[b]	On 10 mesh	25.7	74.3	71.6
	Through 65 mesh	65.3	34.7	76.6
0.01	On 10 mesh	22.8	77.2	57.9
	On 65 mesh	44.7	55.3	65.5
	Through 65 mesh	79.8	20.2	77.3
0.1	On 10 mesh	1.7	98.3	60.2
	Through 65 mesh	3.8	96.2	71.1

[a]Percentage of the actual PCB recovered.

[b]Approximate critical micelle concentration for Triton X-100.

Data in Table V show the effect of varying concentrations of Triton X-100 when slurries were extracted in the separatory funnel before filtration. Thus, these data were obtained using the same isolation procedures used for Table II. The goal of this work was to find a concentration of Triton X-100 which, when added to a slurry, would permit essentially all of the PCB to be extracted in the separatory funnel. Addition of the surfactant would simplify

analysis by obviating the necessity of a separate alcoholic KOH reflux to remove PCB from the fibers.

TABLE V

EFFECT OF TRITON X-100 CONCENTRATION ON PCB REMOVAL BY LIQUID-LIQUID EXTRACTION

Concentration, %	Fibers	Extracted by Separatory Funnel, %[a]	Remaining on Fibers, %[a]
None	On 10 mesh	100	0
	Through 65 mesh	81.8	18.2
0.003	On 10 mesh	97.3	2.7
	Through 65 mesh	85.5	14.5
0.01	On 10 mesh	100	0
	On 65 mesh	100	0
	Through 65 mesh	90.5	9.5
0.1	On 10 mesh	100	0
	Through 65 mesh	100	0

[a]Percentage of the actual PCB recovered.

Immediately evident is the ease with which PCB's were extracted from the slurries containing softwood long fibers and fines with no added surfactant (Table V) in contrast with the hardwood pulp and pulp substitute (Table II). Triton X-100 at 0.1% concentration facilitated complete separatory funnel extraction of PCB's from the slurry of softwood fines. However, the large amount of surfactant added to the sample caused formation of a gel in the separatory funnel which was difficult to manipulate during extraction. In terms of sample handling and extraction efficiency, addition of Triton X-100 at 0.01% concentration based upon the slurry appeared to be the best compromise. Therefore, that surfactant addition has been tentatively recommended as the first step in the routine determination of PCB's in paper mill effluents and fiber slurries. Further studies

will be needed to confirm its utility in samples containing hardwood fibers, pigments, and other suspended material.

PCB LOSSES DURING ANALYSIS

As described in the preceding section of the report, recoveries of known amounts of Aroclor 1242 added to slurries (spikes) ranged from about 60 to 80%. Investigations were, therefore, undertaken to identify points in the isolation and analysis procedure where significant amounts of PCB could be lost.

After confirming that the expected amounts of Aroclor 1242 were actually added to fiber slurries, earlier studies (10) were repeated to demonstrate minimal PCB losses during routine manipulations such as sample cleanup and concentration of petroleum ether solutions on the rotary evaporator. Because 15% methylene chloride in hexane had been shown to possess no advantage in extraction efficiency, petroleum ether was adopted for use in separatory funnel extractions.

Over half of the Aroclor 1242 on the fibers was lost when they were allowed to air dry prior to alcoholic KOH reflux. Thus, in order for alcoholic KOH to be useful for recovering PCB from the fibers, they would have to remain wet following filtration. It was feared, however, that the water remaining on the wet fibers would inhibit complete extraction of the PCB. Three types of treatments were used in the search for residual PCB on the fibers after alcoholic KOH reflux: (1) a second alcoholic KOH reflux, (2) Soxhlet extraction of the fibers with acetone-hexane (59:41), (3) solution of the fibers in 72% sulfuric acid followed by dilution with water and extraction with petroleum ether. Because significant residual PCB was not found in any of these treatments, it was concluded that single alcoholic KOH reflux could adequately remove PCB's from wet fibers. [Earlier work had indicated that a single alcoholic KOH treatment

removed only 85% of the Aroclor 1242 from paperboard (10). Apparently it is more difficult to extract the PCB from a dried paperboard sample than from the loose mat of wet fibers described above.]

Aroclor 1254 has consistently demonstrated higher spike recoveries than Aroclor 1242. Because of its greater average degree of chlorination, Aroclor 1254 is less volatile than Aroclor 1242. Although it had already been shown that there were insignificant PCB losses from petroleum ether and other solvent solutions, the possibility that Aroclor 1242 could be lost by volatilization from aqueous solutions appeared worthy of investigation.

A 250-ml sample of distilled water was spiked with 20 µg Aroclor 1242. Two 100-ml aliquots were withdrawn; one was transferred into a flask at room temperature and extracted immediately to serve as a control, and the other was placed on the rotary vacuum evaporator for one hour at room temperature. The Aroclor 1242 content of the sample which had been on the evaporator was found to be 15% of that in the control sample (85% loss), and its chromatogram showed a dramatic loss of the more volatile constituents. In a repeat of this study, 50% of the Aroclor 1242 was lost from the sample on the evaporator. Only about 10-15 ml of water were removed from the samples during the one-hour evacuation.

Although vacuum evaporation represents a rather extreme treatment for the aqueous samples, the quantitative results and the appearance of the chromatograms strongly suggest that Aroclor 1242 was lost by volatilization. The large loss of Aroclor 1242 during air drying of isolated fibers, discussed previously, also appears to be consistent with this finding. Support in the literature for these experimental results is provided by the report that p,p'-DDT, whose GC retention time is longer than that of any of the PCB isomers in Aroclor 1242,

codistills with water at 25-35°C (28). Reported to contribute to DDT volatilization is its heterogeneous distribution in a sample and accumulation on the upper surface of the water. A theoretical computation of vaporization loss has indicated that the half-life of Aroclor 1242 in a well-mixed stream of 1 m depth is 5.96 hr (29).

PCB losses by volatilization might occur at several points in the sampling and analysis of an effluent. In general, it would seem advisable to minimize manipulations and exposure of the sample to the air. If addition of Triton X-100 to fiber slurries permits elimination of filtration and separate treatment of the fibers, improved PCB recovery as well as reduced analysis time might be realized. Although experimental verification is needed, another potential benefit of the added surfactant would be to reduce PCB concentration at the air-water interface if PCB's behave similar to DDT.

Significant losses of Aroclor 1242, possibly due to volatilization, have made quantitative recovery of PCB spikes difficult to achieve even in distilled water. However, quantitative recoveries were obtained (102.8 and 101.2% in duplicate runs) when the samples were extracted immediately after addition of the spike. One liter of distilled water was placed in a 2-liter separatory funnel. Ten micrograms of Aroclor 1242 in alcohol solution were added, the funnel was swirled slightly, 60 ml of petroleum ether were added, and the separatory funnel was capped and shaken immediately. When the spiked aqueous solution was permitted to sit for one hour before addition of the petroleum ether and extraction, recovery dropped to 91.7%. However, a sample to which the petroleum ether was added immediately after the spike and then permitted to sit for one hour had a recovery of 99.0%. Although the quiescent petroleum ether layer undoubtedly

extracted some of the PCB during the hour, it might also have improved recovery by sealing the air-water interface and blocking PCB volatilization.

PCB sorbed onto the separatory funnel was sought following each of the above runs involving a one-hour wait. The funnels were rinsed with acetone and the acetone analyzed by electron capture gas chromatography (ECGC), but no PCB was detected.

SAMPLE PRESERVATION

The effective preservation of paper mill effluents for subsequent PCB determination is the subject of current concern and active investigation. Water samples containing PCB's were thought to be quite stable until Bellar and Lichtenberg demonstrated that PCB's could be lost and that the loss could be prevented by adding formaldehyde (16). Although formaldehyde would be expected to protect samples against microbiological attack, its mode of action in preserving PCB samples might not be that straightforward.

Preservation techniques can be more efficiently designed if the analyst knows what he is preserving against. As discussed above, PCB loss by volatilization seems to be a significant threat to sample integrity. Minimizing this loss can perhaps be achieved most simply by filling sample containers completely with little or no air space under the aluminum foil-lined lid and analyzing as soon as possible.

Mercury, another material which is lost from samples by volatilization, is more stable in samples containing suspended solids (30). Apparently, stability is facilitated by sorption onto suspended solids. This same phenomenon may affect the stability of PCB's. Reduced vaporization loss of Aroclor 1254 has been

reported when it is strongly sorbed onto a high organic content soil (31). In Tables III and IV total recovery values for Aroclor 1242 in samples containing fines are consistently higher than in samples containing long fibers. The suspected greater PCB sorption on the fines may have enhanced sample stability and caused the higher observed total recovery. Investigations are continuing in this laboratory on this and other facets of the problem of stability and preservation of paper mill effluents for PCB determination.

CONCLUSIONS

1. Perchlorination is not a suitable means for confirming the presence or quantity of PCB's in effluents from mills using secondary fiber. Materials which originally do not contain chlorine might be incorrectly reported as PCB's following perchlorination.

2. Oxidation with chromium trioxide was found to be the most effective technique for removing materials from pulp and paper mill effluents and sludges which interfere with PCB determinations by gas chromatography.

3. Even after chromium trioxide oxidation, some peaks which were determined not to be PCB's remained on some chromatograms of PCB's isolated from mill effluents. These peaks should be ignored in interpretation and quantitation of PCB chromatograms.

4. The distribution of PCB's between water and cellulose fibers was affected by the surface area of the fibers. Fines, with high hydrodynamic specific surface, sorbed more PCB than did long fibers.

5. Small amounts (<0.01%) of a typical nonionic surfactant, Triton X-100, had only a small effect on the distribution of Aroclor 1242 between fibers and water. Larger amounts (>0.01%) promoted removal of PCB from a fiber slurry by separatory funnel extraction. Removal was more difficult from fines than from fibers. Addition of Triton X-100 to fiber slurries prior to separatory funnel extraction should obviate the necessity of a separate alcoholic KOH reflux to remove PCB from the fibers.

6. Volatilization appears to be a mechanism by which significant quantities of Aroclor 1242 have been lost from aqueous samples. Large losses have occurred when wet cellulose fibers are permitted to air dry. Higher PCB recoveries should result when analyses incorporate minimized manipulations and exposure of wet samples to the air.

7. Samples containing fines have demonstrated better total PCB recovery than those containing long fibers. Improved recovery may reflect greater sample stability, which in turn might result from the PCB's having been sorbed onto the fines during sample preparation.

RECOMMENDATIONS

Hopefully, improved analytical accuracy and reduced between-laboratory variation will result from implementation of the findings of this study. Many of these results are incorporated in a recommended procedure for determining PCB's in pulp and paper mill effluents and process streams, the main features of which are listed below. Details of the procedure are in Appendix I. Although this embodies the presently recommended methodology, progress in this and other laboratories could significantly change parts of the procedure virtually overnight.

PROCEDURE FOR PCB'S IN EFFLUENTS

1. Add 0.01% Triton X-100 to sample.
2. Extract 3 times in separatory funnel with hexane, petroleum ether, or 15% methylene chloride in either of above solvents.
3. Clean up extracts on Florisil or alumina.
4. Analyze extracts by electron capture gas chromatography. Ignore peaks which do not conform to a known Aroclor pattern in both retention time and relative peak height.
5. If chromatogram indicates interferences, use chromium trioxide oxidation and return to Step 3.

Note: If the Triton X-100 addition is found not to be generally useful, insert filtration and alcoholic KOH reflux of isolated suspended solids (if present in sample) at end of Step 2.

PROPOSED FUTURE WORK

1. Confirm effectiveness of Triton X-100 addition on a large number of types of samples.

2. Evaluate more completely the significance of PCB losses due to volatilization.

3. Determine the effectiveness of sample preservatives in the presence of cellulose fibers.

4. Evaluate PCB isolation techniques and distribution between water and solid in the presence of other suspended solids (pigments, etc.).

5. Conduct collaborative studies in which several laboratories use the recommended procedure for determining PCB's in samples known to contain interferences.

6. Investigate the mechanism by which surfactants assist in PCB removal from slurries.

7. Determine the amount and effect of PCB which might remain in intact carbonless copy paper capsules in paper mill effluents and samples from within the mill.

ACKNOWLEDGMENTS

The cooperation of Stanton Kleinert and Tom Gibson in arranging analysis of a sample by gas chromatography — mass spectrometry at the Wisconsin Laboratory of Hygiene is gratefully acknowledged.

LITERATURE CITED

1. Proceedings, National Conference on Polychlorinated Biphenyls. (November 1975, Chicago, Illinois). Washington, DC, Environmental Protection Agency, 1976. 471 p.

2. Willford, W. A., Hesselberg, R. J., and Nicholson, L. W., Ref. (1), p. 177-81.

3. Jelinek, C. F., and Corneliussen, P. E., Ref. (1), p. 147-54.

4. Humphrey, H. E. B. Evaluation of changes in the level of polychlorinated biphenyls (PCB) in human tissue. Final report on FDA Contract 223-73-2209. Michigan Dept. of Public Health, Lansing, Michigan, 1976.

5. Trout, P. E., Ref. (1), p. 359-61.

6. Hutzinger, O., Safe, S., and Zitko, V. The chemistry of PCB's. p. 197-220. Cleveland, Ohio, CRC Press, 1974.

7. Eichelberger, J. W., Harris, L. E., and Budde, W. L., Anal. Chem. 46(2): 227-32(Feb., 1974).

8. Young, S. J. V., Finsterwalder, C. E., and Burke, J. A., J. Assoc. Offic. Anal. Chem. 56(4):957-61(1973).

9. Finsterwalder, C. E., J. Assoc. Offic. Anal. Chem. 57(3):518-21(1974).

10. Easty, D. B. Unpublished work, 1976.

11. Ref. (6), p. 211.

12. Webb, R. G., and McCall, A. C., J. Chromat. Sci. 11:366-73(July, 1973).

13. Fairless, W. Testimony given at hearing to consider Wisconsin Department of Natural Resources Administrative Code proposals for controlling polychlorinated biphenyls. August 28-29, 1975, Madison, Wisconsin.

14. Federal Register 38(199), Part II:28758-60(Oct. 16, 1973).

15. Mieure, J. P. Personal communication, 1976.

16. Bellar, T. A., and Lichtenberg, J. J. In Water quality parameters. Special Technical Publication 573, p. 206-19. Philadelphia, American Society for Testing and Materials, 1975.

17. Huckins, J. N., Swanson, J. E., and Stalling, D. L., J. Assoc. Offic. Anal. Chem. 57(2):416-17(1974).

18. Glass, G., Johnson, J., Johnson, L., and Sturino, E. Personal communication, 1976.

19. Sturino, E. Personal communication, 1976.

20. Pesticide Analytical Manual (1968). Vol. 1, 2nd ed. U.S. Food and Drug Administration. Revised April, 1971. Sec. 211.14 (a).

21. Monsanto Methodology for Aroclor. October, 1971.

22. Young, S. J. V., and Burke, J. A., Bull. Environ. Contam. Toxicol. 7:160-7 (1972).

23. Holmes, D. C., and Wallen, M., J. Chromat. 71:562-3(1972).

24. Trotter, W. J., J. Assoc. Offic. Anal. Chem. 58(3):461-5(1975).

25. Munson, T. O., Palmer, H. D., and Forns, J. M., Ref. (1), p. 218-29.

26. Ingmanson, W. L., and Whitney, R. P., Tappi 37(11):523(1954).

27. Dubey, G. A. Unpublished work, 1976.

28. Acree, F., Jr., Beroza, M., and Bowman, M. C., J. Agr. Food Chem. 11(4):278-80 (1963).

29. Mackay, D., and Wolkoff, A. W., Environ. Sci. Technol. 7(7):611-14(July, 1973).

30. Carter, M. J., Huston, M., Jirka, A., and Fuller, F. Preservation of southern Lake Michigan water. Paper presented at American Chemical Society Tenth Great Lakes Regional Meeting, Evanston, Illinois, June 17-19, 1976.

31. Haque, R., Schmedding, D. W., and Freed, V. H., Environ. Sci. Technol. 8(2):139-42(Feb., 1974).

THE INSTITUTE OF PAPER CHEMISTRY

Bette A. Wabers

Bette A. Wabers, Research Assistant

Dwight B. Easty

Dwight B. Easty, Research Associate
Division of Natural
Materials & Systems

Approved by:

Hardev Singhengal

Hardev S. Dugal, Director
Division of Industrial &
Environmental Systems

APPENDIX I

DETERMINATION OF POLYCHLORINATED BIPHENYLS (PCB'S) IN PAPER MILL EFFLUENTS

PCB's are isolated from effluents by liquid-liquid extraction, cleaned up on Florisil-alumina, and determined by gas chromatography. Emulsions, which frequently form during extraction of effluents, are broken by centrifugation. The extraction procedure is similar to that recommended by the Environmental Protection Agency (EPA) for organochlorine pesticides (14). Because pesticides occur rarely in paper mill effluents, two principal features of the method described herein are different from the current EPA method for PCB's in industrial effluents: (1) Samples are extracted with petroleum ether rather than methylene chloride-hexane. (2) No effort is made to separate pesticides from PCB's.

APPARATUS

Disposable pipets (230 mm).

Separatory funnels, Squibb-type, with Teflon stopcocks, 125 and 2000 ml. The 2000-ml separatory funnel should have a stopcock bore of at least 6 mm.

Glass tubes 22 mm OD drawn to a tip with OD about 4 mm at one end and with a length of 25 cm exclusive of the tip.

Rotary evaporator (all glass Rotavapor).

Laboratory centrifuge capable of holding 250-ml bottles.

A gas chromatograph equipped with an electron-capture detector, a 1/8-inch by 4-foot stainless steel column packed with 3% OV-17 on acid-washed and dimethyldichlorosilane-treated Chromosorb W, 80/100 mesh. Instrument conditions:

injector temperature 225°, column temperature 210°, detector temperature 225°, carrier gas flow 25 ml per minute. Other columns are acceptable, including 1/8-inch by 6 feet packed with 4% SE-30/6% OV-210.

A strip chart recorder equipped with a Disc Integrator.

SOLVENTS AND REAGENTS

Petroleum ether suitable for pesticide residue analysis (b.p. 30-60°) (Burdick and Jackson Laboratories, Inc., Muskegon, Michigan).

2,2,4-Trimethylpentane (Iso-octane) (Burdick & Jackson).

Activated Florisil, PR grade, 60/100 mesh (Floridin Co., Berkeley Springs, West Virginia).

Alumina, adsorption, 80/200 mesh (Fisher Scientific Company, catalog No. A-540).

Sodium sulfate, granular anhydrous, reagent grade.

Triton X-100 (Rohm & Haas). Prepare 10% solution in alcohol.

STANDARD SOLUTIONS

Iso-octane solutions of Aroclor 1242 and Aroclor 1254 containing 0.04, 0.2, 0.5, 1, and 2 µg/ml.

ISOLATION OF PCB's

Add 1 ml of Triton X-100 solution to 1 liter of sample. Mix thoroughly. (For convenience in handling, smaller samples of fiber slurries may be taken for analysis.) Place sample in a 2-liter separatory funnel. Add 60 ml petroleum

ether and shake vigorously for 2 minutes. Allow the phases to separate. Paper mill effluents containing suspended matter usually form an emulsion in the upper phase at this point. If no emulsion has formed, follow Procedure A below. Use Procedure B if the sample forms an emulsion.

Procedure A

Transfer the petroleum ether layer to a 250-ml Erlenmeyer flask. Add a second 60-ml aliquot of petroleum ether to the aqueous phase, shake, allow the phases to separate, and add the petroleum ether layer to the Erlenmeyer. Extract with a third 60-ml aliquot of petroleum ether as before. Combine the three petroleum ether extracts, and discard the sample.

Procedure B

Draw off and retain the lower phase. Transfer the emulsion to a 250-ml centrifuge bottle(s), and centrifuge for 5-7 min at 550 × g. Pipet the clear petroleum ether layer into an Erlenmeyer. Solid anhydrous sodium sulfate may be added to help break any remaining emulsion. Centrifuge again after adding the sodium sulfate, and draw off the additional petroleum ether by pipet. Return the lower phase from the centrifuge bottle to the separatory funnel with the lower (aqueous) phase from the original extraction. Add a second 60-ml aliquot of petroleum ether to the separatory funnel, extract, separate phases, and centrifuge the emulsion as before. Repeat the extraction and centrifugation with a third 60-ml aliquot of petroleum ether. Combine the petroleum ether extracts and discard the extracted sample.

CLEANUP OF EXTRACTS

Prepare a 5-cm column of anhydrous sodium sulfate on a cotton plug in a 25 cm by 22-mm OD glass tube. Pour 20-30 ml petroleum ether through the column.

Then dry the combined extracts from the sample by pouring them through the sodium sulfate column and catching the column eluate in a round-bottom flask. Rinse well with petroleum ether the Erlenmeyer which had contained the combined extracts and pour these washings through the drying column. Concentrate the column eluate to about 25 ml on the rotary evaporator. Quantitatively transfer the petroleum ether solution to a 125-ml separatory funnel.

Place a cotton plug in one of the 25-cm glass tubes and add sufficient Florisil to give a 2.5-cm column after tapping. (Previously heat the Florisil for 5 hr or longer at 130°C, and reheat any Florisil that has been kept at room temperature for 24 hr or more.) On top of the Florisil, pour an additional 2.5-cm column of alumina. Pour a 2-cm column of anhydrous sodium sulfate on top of the alumina column. Mount the separatory funnel containing the petroleum ether extractives above the column. Add 40 ml petroleum ether to the column, then add the petroleum ether extractives from the separatory funnel, and finally elute the column with 200 ml of petroleum ether. Make the above additions one after another such that the column does not run dry. Discard the first effluent, but start collecting the effluent as soon as the PCB solution is added to the column. Concentrate the effluent from the column to about 3 to 6 ml. Transfer the solution to a 10-ml volumetric flask and dilute to 10 ml with petroleum ether. Determine PCB in the solution by gas chromatography.

GAS CHROMATOGRAPHY

Inject 5-µl samples of both the standard and the unknown solutions. If necessary, dilute the sample so that its response falls within the range of the available standards. To insure a valid measurement of the PCB in the sample, the size of the peaks from the sample and the standard should be within ± 25%. Measure

chromatogram area or heights of major peaks. Use only those peaks which correspond to a known Aroclor in both retention time and relative peak height. If other peaks obscure the chromatogram, treat with chromium trioxide as described in Appendix II. Quantitate on the basis of a direct proportion between responses of sample and standard.

NOTE

If Triton X-100 is found not to promote complete removal of PCB from suspended solids in the sample during separatory funnel extraction, residual PCB can be removed by alcoholic KOH reflux, as described below. In order to use this procedure, the aqueous sample must be retained following the separatory funnel extraction.

Filter the aqueous sample through paper. Discard the filtrate, and place the residue and filter paper in a 125-ml Erlenmeyer flask. Add 25-35 ml of 2% alcoholic KOH, connect to an air condenser, and reflux gently for 30 min on a hot plate. Place an inverted beaker on the mouth of the flask and allow to cool to room temperature. Transfer the solution to a 125-ml separatory funnel, using 4 10-ml portions of petroleum ether to wash the Erlenmeyer and the residual solids. To assure that all PCB has been transferred to the separatory funnel, use a glass tamper to express the petroleum ether out of the paper and fibers. Add 20 ml water to the separatory funnel and shake well. Drain the lower layer into a second separatory funnel and extract it with 20 ml petroleum ether. Discard the water layer. Combine the two petroleum ether solutions and wash with 3 20-ml portions of water.

Clean up the petroleum ether solution with Florisil-alumina as described above and analyze by gas chromatography.

APPENDIX II

CHROMIUM TRIOXIDE OXIDATION

This procedure is normally applied to sample extracts which have been cleaned up on Florisil and/or alumina, analyzed by electron capture gas chromatography, and found to contain materials which interfere with interpretation of the chromatogram.

REAGENTS AND APPARATUS

The chromium trioxide used was Mallinckrodt CrO_3 powder. Other reagents and apparatus used are discussed in Appendix I.

PROCEDURE

Pipet 2.0 ml of cleaned up petroleum ether extract into a 15-ml graduated centrifuge tube. Add 2.0 ml glacial acetic acid. Place the centrifuge tube in an empty 150-ml beaker on top of a steam bath, with a gentle stream of nitrogen directed at the top of the tube. Care should be taken not to direct the nitrogen stream above the tube. Concentrate in this manner until only the acetic acid remains (about 2 hours).

Add 100 mg of chromium trioxide powder and a small glass bead. After shaking gently, place the tube in a boiling water bath for 20 minutes. The liquid level in the tube should not be below the water level during this heating period.

Remove sample from water bath, cool thoroughly, and transfer to a 125-ml Squibb separatory funnel. Rinse the centrifuge tube twice with 5 ml petroleum ether and add to the separatory funnel. Shake vigorously for 1 minute. During

this period it may be necessary to cool the separatory funnel with an ice-cold towel.

Neutralize the acetic acid by adding 7 ml of 5N NaOH dropwise with cooling and swirling. When the addition is complete, shake vigorously for 1/2-1 minute.

Separate the layers. Remove the top layer with a disposable pipet and put it through a prewashed cleanup column (ID approximately 10 mm) of 1 cm anhydrous sodium sulfate, 2 cm alumina, and 2 cm activated Florisil (in that order, top to bottom). Extract two more times with 10 ml of petroleum ether and put extracts through the column. Elute with 150 ml of petroleum ether.

Concentrate the petroleum ether extracts to 1 ml on a rotary evaporator. Bring up to volume in a 2-ml volumetric flask for injection into the gas chromatograph.

Four to six samples can conveniently be worked up at the same time.

APPENDIX III

PERCHLORINATION OF WATER SAMPLES

This procedure represents the combined recommendations of several investigators (17,18). Although it quite likely will work on extracts from clean water samples, its use has not met with success here because it was applied only to mill effluents. As noted earlier in this report, perchlorination has not been recommended for use on effluents from mills using secondary fiber.

Samples on which this procedure is used have usually been isolated from water by solvent extraction and cleaned up through Florisil or alumina, as described in Appendix I. For minimized losses during concentration, individual samples should contain at least 100 ng Aroclor 1016 or 1242.

APPARATUS AND REAGENTS

Apparatus and reagents are discussed in Appendix I with the following additions:

13 × 100 mm Pyrex culture tubes with screw caps and Teflon cap liners cut from Teflon sheeting.

Glass tubes drawn from 10-mm OD pyrex test tubes for small drying columns.

Gas chromatograph equipped with a ^{63}Ni or $Sc^{3}H$ electron capture detector and a 1/8-inch × 2-foot stainless steel column packed with 3% OV-17. Conditions are column temperature 240°C, injector and detector temperatures 275°C and nitrogen flow of 45 ml/min.

Heating block maintained at 180°C, or

Oven and sand bath at 150°C.

Chloroform, reagent grade.

Antimony pentachloride (Matheson, Coleman and Bell or Baker).

Hydrochloric acid, 6N.

Benzene (Burdick and Jackson).

PROCEDURE

Place 2 ml of cleaned up petroleum ether extract containing the suspected PCB into a culture tube. Concentrate to 1 ml at room temperature by directing a gentle stream of nitrogen at the top of the tube. Do not apply any heat during concentration. Add 2 ml $CHCl_3$ and concentrate, as described above, to near dryness. Add 2 ml more $CHCl_3$ and concentrate to 0.5 ml.

Add 0.2 ml antimony pentachloride and immediately cap the culture tube with a Teflon-lined cap. Allow the reaction to proceed 4 hr in an aluminum heating block at 180°C or overnight in a sand bath in an oven at 150°C.

Cool the reaction tube to room temperature. Immediately but slowly add 0.5 ml 6N HCl. Add 2.0 ml warm (50°C) benzene and shake vigorously. Remove the benzene layer with a disposable pipet and put it through a prewashed drying column containing 2 grams anhydrous sodium sulfate. Repeat this extraction 2 more times, collecting extracts in a 50-ml round bottom flask. Wash column with 10 ml warm benzene.

On the rotary evaporator, concentrate the combined extracts and the column wash to 5 ml. Add 2 ml petroleum ether and concentrate almost to dryness. Dilute with petroleum ether to a known volume and analyze for decachlorobiphenyl by gas chromatography.